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14. ABSTRACT

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

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Design of Energetic Ionic Liquids

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Abstract

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds which can potentially meet these requirements is known as ionic Liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine—which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

1. Introduction

The design of new high energy density materials, which are more efficient, reliable, and environmentally benign than existing rocket propellants, is a high DoD priority. The focus of this effort has been on the development of new propellants and energetic additives, including highly strained hydrocarbons, polynitrogen compounds, and advanced monopropellants. Some of the issues that must be addressed in theoretical efforts to design new energetic materials include an assessment of their energy content, their thermodynamic and kinetic stability, and the design of new synthetic routes to proposed new compounds that have not yet been synthesized.

A specific area of interest to the DoD is the discovery of a suitable replacement for hydrazine, a widely used monopropellant for low-thrust propulsion applications such as orbital maneuvering and satellite stationkeeping. The desire to replace hydrazine is motivated by several factors. Perhaps the most severe limitation of hydrazine is its carcinogenic nature and extreme respiratory and dermatological toxicity, with correspondingly large costs associated with controlling these environmental and biological hazards. Furthermore, the performance of hydrazine as a monopropellant is rather modest due to its relatively low density and specific impulse compared to a prototypical ionic monopropellant salt such as 4-amino-1,2,4-triazolium dinitramide. The replacement of hydrazine with more energetic, less hazardous energetic monopropellants is clearly needed.

A specific type of energetic material of current interest is derived from a broad class of compounds known generically as ionic liquids (ILs), which are chemical salts with unusually low melting points; e.g., below 100° C. The general interest in ILs has focused mainly on their use as environmentally benign ("green") solvents for a wide range of chemical reactions. Some of the properties of ILs which make them attractive as solvents include their low vapor pressure, large liquid ranges, and thermal stability. The interest in ILs as new monopropellants stems from several factors. For example, the properties of ILs, including their energy content, can be "tuned" through a judicious choice of component ions and their substituents. Furthermore, the virtually nonexistent vapor pressure of ILs greatly reduces the environmental and biological hazards due to respiratory and dermatological toxicity. Finally, the densities of ILs generally are significantly greater than those of conventional liquid monopropellants such as hydrazine.

Although there have been extensive experimental studies of chemical reactions in ILs, little has been done in the area of characterization of the fundamental chemical and physical properties of ILs. In particular, one of the most pressing needs in the broader area of IL development, and particularly in the design of energetic ILs, is the application of robust theoretical methods for the reliable prediction of IL heats of formation, synthesis routes, phase transitions, ion conformations, thermal stabilities, densities, and viscosities. The focus of this study is on the characterization, design, and synthesis of the next generation of monopropellants for rocket propulsion applications.

2. Computational Methods

An integrated approach utilizing multiple computational methods is used to predict and characterize the intrinsic and bulk properties of energetic ionic liquids. At the molecular level, highly accurate electronic structure methods are used to predict the fundamental properties of the ionic liquid components, including molecular structures, charge delocalization, heats of formation, and proton transfer reaction pathways and barriers. Geometries, electronic structures, and properties (including heats of formation) of the component ions are predicted using second-order perturbation theory (MP2, also known as MBPT(2)[1]), density functional theory (DFT)[2], coupled cluster theory (CCSD(T)[3]) and the "Gaussian-N" (GN)[4] methods. The Nuclear-Electronic Orbital (NEO)[5] approach is used for capturing the quantum dynamical effects of hydrogen bonding and proton transfer. The Fragment Molecular Orbital (FMO) method[6], which decomposes a large molecular system (e.g., a cluster, protein, liquid, zeolite, etc.) into small subunits (fragments) that are designed to both retain the high accuracy of the chosen quantum mechanical level of theory while greatly reducing the demands on computational time and resources, is used in studies of ion clusters. In addition, the complex spectrum of ionic liquid physical properties requires utilization of atomistic molecular dynamics and coarse-grained condensed phase simulations in order to obtain reliable predictions of many key bulk properties.

GAMESS,[7] the primary quantum chemistry code used in this study, is highly scalable. For example, the fixed-size parallel efficiency of the GAMESS TI-08 large test case (MP2 gradient, 898 atomic orbitals) on the Cray XT3 at the Engineer Research and Development Center (ERDC) DoD Supercomputing Resource Center is 75% on 1,024 cores (single core mode, relative to 64 cores) and 68% on 2,048 cores (dual core mode, relative to 256 cores). The condensed phase simulations were performed using the scalable LAMMPS classical molecular dynamics code,

which delivers a scaled-size parallel efficiency of approximately 90% on 8,192 cores on a Cray XT3 (see http://lammps.sandia.gov/bench.html)

3. Results and Discussion

[$Emim^+$][Im^-] Ion Clusters: Ionic liquids are promising candidates for electric propulsion working fluids, mainly due to their small vapor pressures, good electrical conductivities, and their ability to be readily sprayed into vacuum. Specific ILs under consideration for this type of application include 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl) imide ([$Emim^+$][Im^-]) and 1-butyl-3-methylimidazolium dicyanamide ([$Bmim^+$][Dca^-]). In order to assess and tune the performance of these types of working fluids, it is necessary to characterize the exhaust plume, which, in the case of the former IL, contains a distribution of clusters such as $[Emim^+]_m[Im^-]_{m\pm1}$; i.e., containing either an excess cation or anion. To aid in the characterization of these ion clusters, the gas-phase structures, harmonic vibrational frequencies, and binding energies of a series of $[Emim^+]_m[Im^-]_n$ (m,n=1-3) clusters were computed at the MP2/6-311++G(d,p)[8] level and compared to earlier density functional theory (B3LYP/6-311++G(d,p)) calculations.[9] Prior B3LYP and MP2 calculations of the structures of the single ion pair [$Emim^+$][Im^-] and ion trimers containing an excess cation ($[Emim^+]_2[Im^-]$) or anion ($[Emim^+][Im^-]_2$) show a consistent difference between predicted structures and binding energies. In particular, the MP2 predicted structures generally favor interactions between the anion and the π electron density of the cation ring, whereas the DFT geometries tend to favor interionic hydrogen bonding between the hydrogen atoms on the cation and the nitrogen or oxygen atoms of the anion. In the present study, this comparison is exended to the larger $[Emim^+]_2[Im^-]_2$ and $([Emim^+]_3[Im^-]_2$ ion clusters, shown in Figures 1 and 2, respectively.

The B3LYP and MP2 predicted structures of $[Emim^+]_2[Im^-]_2$ are shown in panels (a) and (b), respectively, of Figure 1. While the two structures are qualitatively similar, a detailed examination reveals somewhat stronger interionic interactions in the MP2 geometry relative to B3LYP. For example, in the MP2 geometry, 13 hydrogen bonds are present, with bond lengths ranging from 2.05 to 2.57 Å, whereas in the DFT structure there are 11 hydrogen bonds with lengths ranging from 2.14 to 2.60 Å. Similar results are found for the B3LYP and MP2 geometries of $[Emim^+]_3[Im^-]_2$, which are shown in Figures 2a and 2b, respectively.

Due to the cluster sizes and the nature of the relatively weak interactions between the component ions in the $[Emim^+]_m[Im^-]_{m\pm1}$ clusters, calculation of these structures was computationally demanding. Several hundred runs were necessary, each of which utilized 1,024 nodes, resulting in an aggregate requirement of over 10 million cpu hours on the ERDC Cray XT3.

4-Amino-1,2,4-triazolium dinitramide ion clusters: Previous studies of ionic liquids[10] have focused on the decomposition of ion pairs, providing insight into the chemistry of their ignition as high-energy fuels. The focus of this study, however, is to accurately describe larger systems beyond single anion−cation pairs. Recent work by Li et al.[11] has provided an accurate structure of two ion pairs (two cations and two anions), providing a greater understanding of the molecular structure and intermolecular interactions. The same system is modeled here, along with systems of three ion pairs, to illustrate the effectiveness of the FMO method in accurately describing complex molecular clusters, with the goal of modeling much larger systems in the future.

Two ionic liquid systems, 1,2,4-triazolium dinitramide and 4-amino-1,2,4-triazolium dinitramide, were studied using both ab initio MP2 and the MP2 implementation of the FMO method[12] with each ion chosen as a FMO fragment or monomer. Structures composed of two cations and two anions (tetramers) and larger clusters of three cations and three anions (hexamers) were optimized at the MP2/6-31+G(d) level of theory. FMO2-MP2 and FMO3-MP2 single-point energy calculations were then performed for comparison with the fully ab initio results.

Comparing the energies from FMO2 and FMO3, it can be seen immediately that the FMO method captures the total energy very well, within 2 kcal/mol in the worst case (see Table 1). For the tetramers, both FMO2 and FMO3 are in good agreement; the FMO2 errors are less than 1 kcal/mol relative to the fully ab initio results. For the hexamers, the FMO2 errors are less than 2 kcal/mol, illustrating that FMO3 is not required to achieve an acceptable level of accuracy for these particular ionic liquid systems. Whether this trend persists as system size grows beyond three ion pairs, or for other ion pairs, must be tested further.

Another consideration for larger molecular systems is the computer time required. To illustrate the overall effectiveness of the FMO method in both providing accurate results and reducing computational requirements, timings were performed for the ionic liquid systems described above. Due to the fact that FMO2 is in good agreement with the ab initio results, only timings for FMO2 will be shown. However, it is noted here that because

the tetramers and hexamers examined here are small, the FMO3 timings for these systems do no exhibit any time savings relative to the full MP2 calculations. The benefit of using FMO3 is only seen with larger systems.[13] Timings were performed on a Cray XT4 supercomputer using AMD Opeteron64 processors running at 2.1 GHz, located at the U.S. Army Engineer Research and Development Center (ERDC) in Vicksburg, Mississippi. Single-point MP2 energy calculations were performed using 8, 16, and 32 processors with both FMO2 and MP2 using the 6-31+G(d) basis set. As shown in Table 2, FMO2 requires approximately half of the computer time of a full MP2 calculation on the tetramers. With the increase in available processors, the overall time requirements are cut in half for both FMO2 and MP2, showing good scalability for both methods. With an increase in system size from ionic liquid tetramers to hexamers, the computer time required for a fully ab initio calculation increases more than 6 fold, while the FMO2 requirement only doubles. Therefore, the FMO2 cost savings relative to full MP2 is much greater than that observed for the tetramers. Again, scalability for both methods is very good for the hexamers, cutting the computational time in half when doubling the number of available CPUs. It is apparent that as the system size increases to larger ionic liquid clusters or as the basis set size increases (or both), the computational requirements for a fully ab initio calculation will rapidly and increasingly exceed those for FMO2. It may be that as the system size increases, the importance of three-body contributions to the interaction energy will also increase, requiring the use of FMO3. Future work will determine the importance of three-body terms in ionic liquid systems, as well as the ability of the FMO method to describe larger molecular clusters.

Large Scale Molecular Dynamics and Coarse-grained Simulations of Ionic Liquids: Atomistic and coarse-grained MD simulations were designed and performed to study the structure and dynamical properties of room temperature ionic liquids (ILs). Eight papers were published[14-21] over the last two years on this topic, including a review[16] in a Special Issue of Accounts of Chemical Research devoted to ionic liquids. As one example of this body of work, the behavior of the ionic liquid/vacuum interface was studied by applying the multiscale coarse-graining (MS-CG) method.[17] When the alkyl chain length of the IL cation was increased, a simple monolayer ordering was shown to change over to a unique multilayer ordering at the IL interface, while the surface tension decreased and approached a constant value, consistent with Langmuir theory[22] and experiment[23,24]. A detailed orientational study demonstrated that the alkyl chain of the IL cations prefers to align parallel to the surface normal while the aromatic ring tends to be perpendicular to the surface normal. The surface electron density profile showed that the surface electron density oscillations are mainly contributed by the cations. Figure 3 (a) through (d) depicts the results for the 1-dodecyl-3-methylimidazolium/NO_3^- system, revealing a clear multilayer ordering. Shown are: (a) all CG sites; (b) CG sites of aromatic rings, the CH_3 groups on long side chains and anions; (c) CG sites of the CH_3 groups on long side chains; and (d) CG sites of aromatic rings and anions. MS-CG models of bulk 1-alkyl-3-methylimidazolium-based (ILs) with alkyl substituents of different lengths were also developed and applied to predict novel nanoscale spatial heterogeneity[15]. Similar results were obtained for water-IL liquid mixtures that exhibited unique nanostructural micelle formation phenomena[14] and for the model energetic ionic liquid HEATN, revealing a pronounced glassy behavior related to this IL's different chemical structure[18].

4. Summary and Conclusions

The structures, harmonic vibrational frequencies, and binding energies of gas-phase ion clusters of the 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid have been predicted using second order perturbation theory (MP2/6-311++G(d,p)) and compared to prior density functional theory (B3LYP/6-311++G(d,p)) results. The MP2 predicted structures generally favor interactions between the anion and the π electron density of the cation ring, whereas the DFT geometries tend to favor interionic hydrogen bonding interactions. However, the difference between MP2 and DFT geometries are less pronounced for larger ion clusters.

The geometries of 1,2,4-triazolium dinitramide and 4-amino-1,2,4-triazolium dintramide ion cluster tetramers (2 cations and 2 anions) and hexamers (3 cations and 3 anions) were optimized at the MP2/6-31+G(d) level of theory. For the tetramers, FMO2 and FMO3 single point energies at the MP2/6-31+G(d) geometries reproduced the full MP2 energies to within 0.69 and 0.03 kcal/mol, respectively. For the hexamers, the corresponding absolute errors in the FMO2 and FMO3 total energies were 1.35 and 0.27 kcal/mol, respectively. Timings on the ERDC Cray XT4 performed using 8, 16, and 32 processors show that FMO2 single point energies for the 4-amino-1,2,4-triazolium dinitramide tetramer require approximately half of the computer time for a full MP2 energy calculation. Furthermore, for the hexamers the computer time for full MP2 increases more than 6-fold whereas for FMO2 the required computer time only doubles.

Large scale MS-CG simulations of the structure of the liquid/vacuum interface in ILs show a transition from a simple monolayer ordering to a unique multilayer ordering at the IL interface as the length of the IL alkyl side chain

is increased. The surface tension decreases and approaches a constant value, consistent with both Langmuir theory and experiment.

Transferable coarse-grained IL force fields were constructed using effective force coarse-graining (EF-CG) methods. A single EF-CG IL model successfully reproduced the structures and properties of other ILs with different side chain lengths. Good transferability over a wide temperature range (298-700K) was also demonstrated.

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Table 1. FMO errors (kcal/mol) for tetramer and hexamer ionic liquid clusters.

	Absolute Error (kcal/mol) 6-31+G(d)	
Tetramers	FMO2-MP2	FMO3-MP2
1,2,4-triazolium dinitramide	0.06	0.02
4-amino-1,2,4-triazolium dinitramide	0.69	0.03
Hexamers		
1,2,4-triazolium dinitramide	0.32	0.07
4-amino-1,2,4-triazolium dinitramide	1.35	0.27

Table 2. Timings for ionic liquid clusters performed on a Cray XT4 with 2.1GHz AMD Opteron64 processors. Each node contains a 4-core CPU and 8 GB of RAM.

		Timing (minutes) 6-31+G(d)	
Tetramer	# CPUs	FMO2-MP2	MP2
4-amino-1,2,4-triazolium dinitramide	8	12.2	28.4
	16	6.4	14.7
	32	3.5	7.3
Hexamer			
4-amino-1,2,4-triazolium dinitramide	8	24.0	172.1
	16	12.5	83.9
	32	6.8	42.8

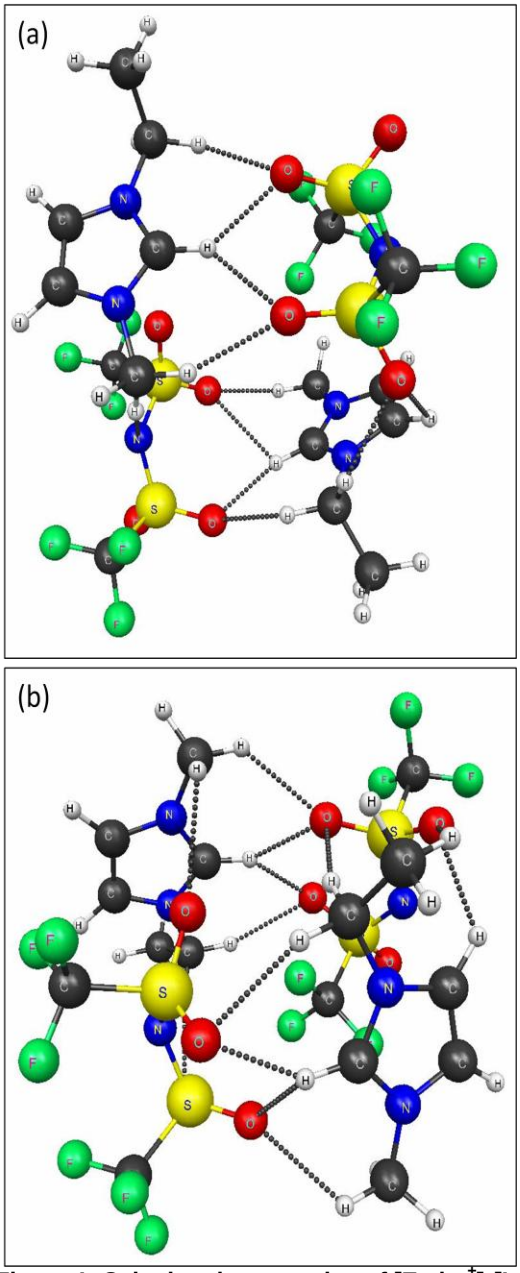

Figure 1. Calculated geometries of $[Emim^+]_2[Im^-]_2$, (a) B3LYP/6-311++G(d,p) and (b) MP2/6-311++G(d,p). H, C, N, O, F, and S atoms are shown in white, black, blue, red, green, and yellow, respectively. Hydrogen bonds are shown as dashed lines.

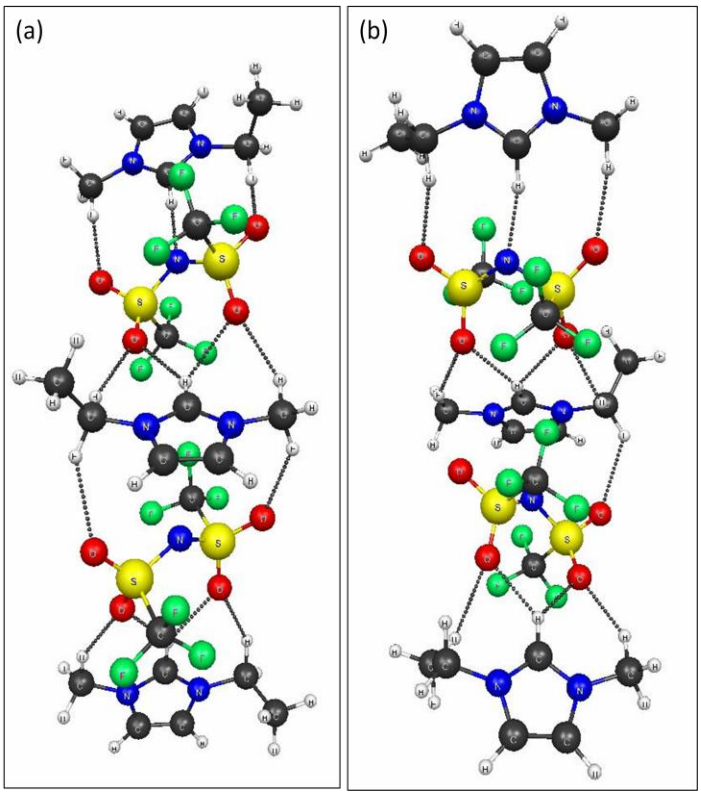

Figure 2. Calculated geometries of $[Emim^+]_3[Im^-]_2$, (a) B3LYP/6-311++G(d,p) and (b) MP2/6-311++G(d,p). H, C, N, O, F, and S atoms are shown in white, black, blue, red, green, and yellow, respectively. Hydrogen bonds are shown as dashed lines.

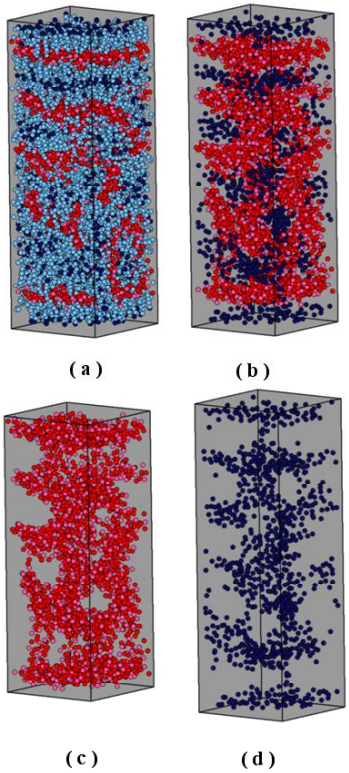

Figure 3. Spatial heterogeneity and charge layering of an IL interface (top layers). See text for details.

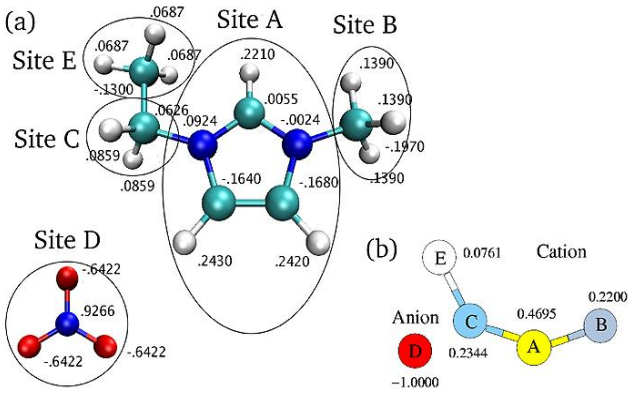

Figure 4. CG model for the (EMIM$^+$)/NO_3^- ionic liquid.

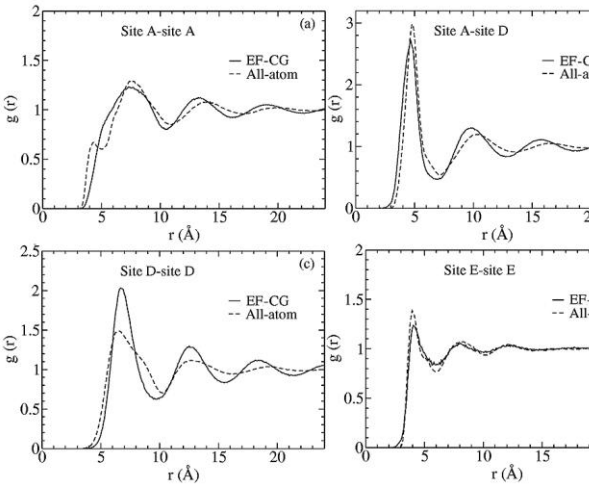

Figure 5. Comparison of RDFs for the EF-CG and all-atom MD simulations for the (EMIM$^+$)/NO_3^- ionic liquid.